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(54) **Process for preparing hydrotreating catalysts prepared from hydrogels and catalysts thus prepared.**

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(73) Proprietor: **SHELL INTERNATIONALE RESEARCH**  
**MAATSCHAPPIJ B.V., Carel van Bylandtlaan 30,**  
**NL-2596 HR Den Haag(NL)**

(72) Inventor: **Kemp, Richard Alan, 11510 Chariot, Stafford**  
**Texas 77477(US)**

(74) Representative: **Aalbers, Onno et al, P.O. Box 302,**  
**NL-2501 CH The Hague(NL)**

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## Description

The present invention relates to a process for preparing alumina hydrogel-derived catalysts, and to catalysts thus prepared, see also EP-A 266 009, 266 010, 266 011 and 266 012.

In the catalytic processing of petroleum feedstocks, it is often desirable to alter the pore structure of the catalyst in order to accommodate different types of feeds. For example, when processing feedstocks with high metals content, the metals tend to deposit rapidly on the catalyst surface and plug the pores of conventional hydroprocessing catalysts, resulting in a loss of catalytic activity for sulphur and nitrogen removal. To facilitate the diffusion of large components into and out of the catalyst and to prevent surface deposits of coke and metals, large pore diameters are required. On the other hand, when processing feedstocks with no metals or with low metals contents, it may be technically and economically desirable to use narrow-pore catalysts. For purposes of denitrification, narrow-pore catalysts have higher activities and longer lives than catalysts containing large pores which tend to deactivate quickly.

The present invention relates to a process for preparing hydrotreating catalysts having surface areas above 300 m<sup>2</sup>/g and at least 80% of the pore diameters less than 5 nm, which process comprises:

(a) precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 and a temperature in the range between 20°C and 90°C, thereby forming a precipitate,

(b) ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.5,

(c) washing the precipitate,

(d) mixing the precipitate with one or more solution(s) containing solubilized salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof and an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a phosphorus-containing compound in an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts on to the gel is sufficient to yield a final catalyst having from 8%w to 32%w heavy metal and from 1%w to 5%w nickel and/or cobalt,

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

It has been found that catalysts prepared from hydrogels aged at high pHs have physical properties better than catalysts prepared from hydrogels aged at lower pHs as well as catalysts prepared by conventional impregnation techniques. Two of the major advantages of the hydrogel route are higher metals utilization and lower costs of catalyst manufacture. The catalysts prepared according to the invention have high surface areas, greater than 300 m<sup>2</sup>/g; high flat plate crush strengths, greater than 90 N; and substantial portions, greater than 80%, of their pores with diameters less than 5 nm. These catalysts are particularly useful for hydrotreating applications.

In the process according to the present invention, a highly active hydrotreating catalyst is prepared by incorporating a metals solution containing an element selected from the group consisting of molybdenum, tungsten and mixtures thereof, an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a phosphorus-containing compound into an alumina hydrogel-derived support.

The process according to the present invention can suitably be carried out by:

(a) titrating an aqueous solution of an acid aluminium salt with an aqueous solution of a basic aluminium compound at a pH in the range between 5.5 and 10.0 and a temperature in the range between 20°C and 90°C, thereby forming a precipitate,

(b) ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.5,

(c) washing the precipitate,

(d) mixing the precipitate with one or more solution(s) containing solubilized salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, and an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a phosphorus-containing compound in an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts on to the gel is sufficient to yield a final catalyst having from 8%w to 32%w heavy metal and from 1%w to 5%w nickel and/or cobalt.

(e) extruding the product of step (d), and

(f) drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

The alumina hydrogel can be prepared by titrating an aqueous solution of one or more aluminum salt(s) with an appropriate acidic or basic material or solution to cause precipitation of the phosphated alumina gel.

The temperature and pH of the precipitation are important variables in the preparation of the aluminas

into which metals solutions can be incorporated to form hydrotreating catalysts with desirable physical qualities. Changes in precipitation temperatures and pHs result in changes in porosities. According to the present invention, a precipitation temperature typically ranges from 20°C to 90°C, and preferably from 50°C to 85°C, and a precipitation pH typically ranges between 5.5 and 10.0, preferably between 5.5 and 8.0, and more preferably between 6.0 and 7.5. The length of time required for the precipitation step is not critical. However, the maximum rate of addition of the aluminium species is fixed by the rate at which the two streams can be mixed and the pH and temperature of the system can be effectively controlled.

In the process according to the present invention the alumina gel can be prepared by titrating an acidic aluminium salt such as, for example, aluminium sulphate, aluminum nitrate or aluminium chloride, in aqueous solution with a basic precipitating medium such as, for example, sodium hydroxide or ammonium hydroxide, or, by titrating an alkali metal aluminate such as, for example, sodium aluminate or potassium aluminate, in aqueous solution with an acidic precipitating medium such as, for example, hydrochloric acid or nitric acid. The adjustment of the pH of an aluminium-containing solution to between 5.5 and 10.0 will result in precipitation of the aluminium as aluminium hydroxide or hydrated aluminium oxide.

In a preferred embodiment, the alumina hydrogel is prepared by titrating an aqueous solution of an alkali metal aluminate and an aqueous solution of an acid aluminium salt to cause precipitation of the alumina gel. The precipitation can be carried out by adding an aqueous solution of the basic aluminium species to an aqueous solution of the acidic aluminium species or the procedure can be reversed by adding an aqueous solution of the acidic aluminium species to an aqueous solution of the basic aluminium species (referred to as "sequential precipitation"). Preferably, the precipitation according to the present invention is carried out by simultaneously adding the acid aluminium species and the basic aluminium species, thus creating a well-defined and constant environment for the precipitation of the hydrogel (referred to as "simultaneous precipitation").

After the precipitation step is completed, the pH of the slurry is adjusted by the addition of the basic aluminate solution to fall in the range from 11.0 to 12.5 preferably 11.0 to 12.0, most preferably 11.5 to 12.0, and aged at a temperature in the range from 20°C to 90°C, preferably 50°C to 85°C for at least 15 minutes. An upper limit on the length of time for ageing is not critical and is normally determined by economical considerations. Ageing times will typically range from 0.1 to 10 hours, preferably from 0.25 to 5 hours, and more preferably from 0.25 to 1 hour. In general, aluminas with acceptable properties are produced by holding the ageing temperature substantially equal to the precipitation temperature. The ageing pH, however, is critical. Products with acceptable pore size distributions are prepared only when the ageing pH is between 11.0 and 12.5, and preferably between 11.0 and 12.0. Compounds prepared at lower pH values contain primarily macropores. The products formed containing macropores have unacceptably low crush strengths. Ageing at excessively high pHs will result in dissolution of the alumina gel.

After ageing, the slurry is washed and filtered in routine fashion to remove substantially all the salts formed during the precipitation of the hydrogel which can be removed by washing. The preferred solvent for washing is water although other solvents such as lower alkanols may be utilized.

After washing, the hydrogel is reslurried with a solution containing solubilized salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, and an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a phosphorus-containing compound an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts onto the gel is sufficient to deposit on the final catalyst from 8%w to 18%w molybdenum or 10%w to 32%w tungsten and from 1%w to 5%w nickel and/or cobalt. When mixtures of molybdenum and tungsten are utilized, the final catalyst contains from 8%w to 32%w molybdenum and/or tungsten. Alternatively, the solution may contain amounts of nickel and/or cobalt and molybdenum or tungsten in excess of that required to deposit the aforesaid amounts of metals, which excess may be removed by washing following the reslurry step. A typical metals solution can be prepared by combining a molybdenum solution with a nickel and/or cobalt solution. A phosphorus-containing compound is typically added to the nickel and/or cobalt solutions in order to prevent formation of unstable nickel and/or cobalt/molybdenum or nickel and/or cobalt/tungsten complexes when the solutions are combined. As used herein, the term "a phosphorus-containing compound" is generic and refers to one phosphorus-containing compound as well as more than one phosphorus-containing compound. The phosphorus-containing compound is suitably phosphoric acid, a phosphate salt or a mixture thereof. Suitable phosphate salts include alkali metal phosphate, alkali metal hydrogen phosphate, ammonium phosphate and ammonium hydrogen phosphate.

The molybdenum solution contains a water-soluble source of molybdenum such as ammonium heptamolybdate or ammonium dimolybdate dissolved in water.

The tungsten solution typically contains ammonium metatungstate dissolved in water. A preferred method for preparing molybdenum and tungsten solutions comprises adding hydrogen peroxide to the appropriate solution in the range of 0.1 to 1.0 mole of hydrogen peroxide per mole of molybdenum or tungsten, respectively. In addition, a suitable soluble amine compound such as monoethanolamine, propanolamine or ethylenediamine may be added to the solutions in order to aid in stabilization of the solutions.

The nickel solution contains one or more nickel salts dissolved in water and a phosphorus-containing compound. A wide range of nickel compounds are suitable, such as nickel nitrate, nickel acetate, nickel

formate, nickel sulphate, nickel oxide, nickel phosphate, nickel carbonate, nickel chloride, and nickel hydroxide. Two compounds that are especially useful are nickel nitrate and nickel carbonate.

The cobalt solution contains one or more cobalt salts dissolved in water and a phosphorus-containing compound. A wide range of cobalt compounds are suitable, such as cobalt nitrate, cobalt hydroxide, cobalt acetate, cobalt oxalate, or cobalt oxide. The preferred cobalt compound is cobalt nitrate.

The temperature and pH of the reslurry step are both important variables in the preparation of hydrogel-derived catalysts which have acceptable densities and porosities. In general, high temperatures in the reslurry step result in lower density catalysts. The pH of the reslurry step, however, is critical to the formation of catalysts having the desired properties. The reslurry of the hydrogel support with the metals solution is carried out at a pH in the range between 4.0 and 8.0, preferably between 4.0 and 6.0, adjusting to these pH ranges by adding, if necessary, acid or base to the hydrogel, the metals solution and/or the mixture of the slurry and the metals solution, and a temperature in the range between 25°C and 100°C, preferably between 25°C and 80°C, until adsorption of the metals salts onto the gel is sufficient to yield a final calcined catalyst having from 8%w to 18%w molybdenum or from 10%w to 32%w tungsten and from 1%w to 5%w nickel and/or cobalt. Reslurry pHs less than 4.0 result in dissolution of the alumina gel and reslurry pHs greater than 8.0 result in failure of the molybdenum or tungsten to adsorb onto the gel. Typically, the times for reslurry will range from 0.5 to 2 hours. Optionally, the resulting material can be washed to remove unadsorbed metals and filtered in routine fashion.

Following the reslurry step, the material may be extruded and then dried and calcined; dried, milled with addition of water, extruded or pelleted and calcined; or partially dried, extruded or pelleted, dried more completely and calcined. Drying is accomplished by conventional means. It may be carried out by forced draft drying, vacuum drying, air drying or similar means. Drying temperatures are not critical and depend upon the particular means utilized for drying. Drying temperatures will typically range from 50°C to 150°C.

In a preferred embodiment, the material is extruded and then dried. Alternatively, the material may be extruded after drying to the proper loss on ignition (LOI). However, to facilitate extrusion, organic binders and/or lubricants may be added prior to extrusion.

After drying, the material is calcined to produce the finished catalyst. The material may be calcined in any atmosphere, reducing, oxidizing or neutral, although air is preferred. However, if binders and/or lubricants are used the material is heated in an oxygen-containing atmosphere, preferably air, in order to burn out the binders and lubricants. Calcining temperatures will typically range from 300°C to 900°C. Typically, burn-out temperatures will range from 300°C to 900°C. Drying, calcining and burn-out may be combined in one or two steps. Most frequently the calcining and/or burn-out steps are combined using an oxygen-containing atmosphere.

Certain other processing steps may be incorporated into the above-described procedure without deviating from the scope and intent of the present invention. For example, prior to the complete drying of the catalyst, it may be extruded and then dried more completely, followed by calcination.

The final catalysts are found to have surface areas greater than 300 m<sup>2</sup>/g, pore volumes ranging from 0.4 to 1.2 cm<sup>3</sup>/g and with at least 80% of its pore volume in pores having diameters less than 5 nm. Crush strengths are greater than 90 N. In general, the metals contents of the final catalysts range from 8%w to 18%w, preferably 10%w to 14%w molybdenum or 10%w to 32%w, preferably 18%w to 26%w tungsten and from 1%w to 5%w, preferably from 2.5%w to 4%w nickel and/or cobalt.

The catalysts prepared according to the present invention can be suitably applied to hydrocarbon conversion processes such as catalytic cracking, hydrocracking, hydrotreating, isomerization, hydrogenation, disproportionation, dehydrogenation, oligomerization, alkylation, dealkylation and the like.

Typical hydroconversion processes utilizing the catalysts according to the present invention will be carried out at a temperature ranging from 150°C to 450°C, a pressure ranging from 14 bar to 175 bar and a liquid hourly space velocity of 0.1 to 10.0 reciprocal hour.

The catalysts according to the present invention are most commonly employed in hydrotreating feedstocks ranging in volatilities from naphthas to flashed distillates.

The invention will now be illustrated by the following Examples.

#### Example 1

Seven hundred and forty grams of reagent grade sodium aluminate were added to 1000 grams of water which was then heated to 60°C in order to effect dissolution of the materials. Five hundred and forty-four grams of aluminium chloride hexahydrate were added to 760 grams of water. Both solutions were cooled to slightly less than 60°C and placed in dropping funnels.

Five thousand grams of water were added to a 10 litre stainless steel bucket equipped with a pH meter, thermometer and stirrer. After the pH was adjusted to 7.0 using the sodium aluminate solution, the two solutions in the dropping funnels were added simultaneously to the well-stirred bucket, maintaining a precipitation pH of 7. A total of 1740 grams of sodium aluminate solution and 1216 grams of aluminium chloride solution were used to effect the titration. After these quantities of reagents had been used, the final ageing pH of the solution rose to between 11.0 and 12.0. The solution was aged for one hour at 60°C. The resulting material was filtered and washed in two large Buchner funnels with about 50 litres of water. The

excess water from the wet filter cake was removed by vacuum. The hydrogel was then divided into two equal portions.

The following solutions were then prepared. 91.71 grams of nickel nitrate as hexahydrate was mixed with 64.59 grams of 85% phosphoric acid and diluted to 1000 millilitres with water. An additional solution of 136.17 grams of ammonium heptamolybdate and 21.21 grams of 30% hydrogen peroxide were diluted to 1000 millilitres with water. The two solutions were combined slowly with stirring and one portion of the hydrogel was added and reslurried with one-half of the solution at 80°C for two hours at a pH of 5.0. At the end of two hours, the slurry was filtered and washed with two litres of water. The excess water from the slurry was again removed by vacuum. The wet gel was then extruded using a small, hand-held extruder using a 4 mm cylindrical die, dried overnight at 120°C and calcined in air at 510°C. The properties of the catalyst (1) are listed in Tables I and II.

#### Comparative Experiment A

A catalyst A was prepared according to Example 1 except that the ageing step was carried out at a pH of 10.0. The properties of the catalyst are listed in Tables I and II.

#### Comparative Experiment B

A catalyst B was prepared using a conventional dry pore volume impregnation technique. A solution suitable for impregnating a gamma alumina carrier was prepared as follows. A first solution was made by adding 19.39 grams of nickel nitrate and 16.18 grams of phosphoric acid to 5 millilitres of water which solution was then heated to 40°C and stirred in order to effect dissolution of the materials. A second solution was prepared by mixing 5.5 millilitres of 30% hydrogen peroxide, 30 millilitres of distilled water and 35.20 grams of ammonium heptamolybdate. The mixture was then heated to 40°C and stirred until all solids were dissolved. When both solutions were at or near ambient temperature, the second solution was slowly added to the first solution while stirring. After cooling and diluting with water to the total pore volume of the support, the solution was added to the gamma alumina support in several small portions with intermediate agitations. The impregnated support was further agitated about 5 minutes, dried for 2 hours at 200°C and calcined in air for 2 hours at 485°C. The properties of the catalyst are listed in Tables I and II.

Table I

Catalyst Properties			
	Example 1	Comparative Experiment A	Comparative Experiment B
Ageing pH <sup>a)</sup>	11.0–12.0	10.0	—
Density g/cm <sup>3b)</sup>	0.72	0.26	0.86
Reslurry pH <sup>c)</sup>	5.0	5.0	—
Surface Area m <sup>2</sup> /g <sup>d)</sup>	428	427	186
Pore Volume cm <sup>3</sup> /g <sup>e)</sup>	0.54	1.39	—
Flat Plate Crush Strength N <sup>f)</sup>	108	36	78.8
%wt. Nickel <sup>g)</sup>	1.2	2.4	2.7
%wt. Molybdenum <sup>h)</sup>	11.8	10.5	13.2
%wt. Phosphorus <sup>i)</sup>	3.4	3.7	3.0

Table II

Catalyst Pore Size Distributions				
	Hg Pore <sup>d)</sup> Size Dist	Example 1	Comparative Experiment A	Comparative Experiment B
5	< 5 nm	86.3	0.8	1.7
	5-7 nm	4.8	0.8	15.3
10	7-10 nm	3.0	11.9	29.3
	10-15 nm	2.8	9.6	40.3
	15-35 nm	2.5	12.5	5.1
	> 35 nm	0.7	64.4	8.4
15	a) Measured using an Orion 231 pH meter and Orion electrodes.			
	b) 209 cm <sup>3</sup> volume fully settled in a graduated cup and weighed.			
	c) Measured using an Orion 231 pH meter and Orion electrodes.			
	d) BET, by nitrogen adsorption/desorption, Micromeritics Digisorb 2500 Instrument.			
	e) By nitrogen adsorption, Micromeritics Digisorb 2500 Instrument.			
20	f) Flat plate, single pellet, extrudate approximately 5 mm in length.			
	g) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.			
	h) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.			
25	i) Weight percent determined by neutron activation analysis or atomic absorption spectroscopy.			
	j) Determined by mercury intrusion, to 4136 bar using a Micromeritics Autopore 9210, using a 130° contact angle and 0.473 N/m surface tension of mercury. Numbers listed are percent pore volume.			
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## Claims

1. A process for preparing hydrotreating catalysts having surface areas above 300 m<sup>2</sup>/g and at least 80% of the pore diameters less than 5 nm, which process comprises:

- precipitating an aqueous solution of one or more aluminium salt(s) by adjusting the pH of said solution to a range between 5.5 and 10.0 and a temperature in the range between 20°C and 90°C, thereby forming a precipitate,
- ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.5,
- washing the precipitate,
- mixing the precipitate with one or more solution(s) containing solubilized salts of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof and an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a phosphorus-containing compound in an amount of from 0.2 to 1.5 moles of phosphorus per mole of heavy metal at a pH in the range between 4.0 and 8.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts onto the gel is sufficient to yield a final catalyst having from 8%w to 32%w heavy metal and from 1%w to 5%w nickel and/or cobalt,
- extruding the product of step (d), and
- drying and calcining the product of step (e) at a temperature ranging from 300°C to 900°C.

2. A process according to claim 1, wherein step a) comprises forming a precipitate by titrating an aqueous solution of an acid aluminium salt with an aqueous solution of a basic aluminium compound at a pH in the range between 5.5 and 10.0 and a temperature in the range between 20°C and 90°C.

3. A process according to claim 1 or 2 wherein the precipitation is carried out at a pH in the range between 5.5 and 8.0.

4. A process according to any one of claims 1-3 wherein the precipitation is carried out at a temperature between 50°C and 85°C.

5. A process according to anyone of claims 1-4 wherein the ageing pH is in the range between 11.0 and 12.0.

6. A process according to anyone of claims 1-5 wherein step d) is carried out at a pH in the range between 4.0 and 6.0.

7. A process according to anyone of claims 1-6 wherein said phosphorus-containing compound is

phosphoric acid, a phosphate salt or a mixture thereof.

8. A process according to anyone of claims 1-7 wherein said catalyst contains from 8%w to 18%w molybdenum and from 2.5%w to 4%w nickel and/or cobalt.

9. A process according to claim 2, wherein step a) comprises forming a precipitate by titrating an aqueous solution of an acid aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, with an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate, at a pH in the range between 5.5 and 8.0 and a temperature in the range between 20°C and 90°C, wherein step b) comprises ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.0, and wherein step d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel or cobalt salts, and phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts onto the gel is sufficient to yield a final catalyst having from 10%w to 14%w molybdenum and from 2.5%w to 4%w nickel or cobalt.

10. A process according to claim 1, wherein step a) comprises precipitating an aqueous solution of an acid aluminium salt selected from the group consisting of aluminium sulphate, aluminium nitrate and aluminium chloride, with an aqueous solution of a base at a pH in the range between 5.5 and 8.0 and a temperature in the range between 20°C and 90°C, thereby forming a precipitate, wherein step b) comprises ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.0, and wherein step d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel or cobalt salts, and phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts onto the gel is sufficient to yield a final catalyst having from 10%w to 14%w molybdenum and from 2.5%w to 4%w nickel or cobalt.

11. A process according to claim 2, wherein step a) comprises forming a precipitate by titrating an aqueous solution of an acid with an aqueous solution of a basic aluminium compound selected from the group consisting of sodium aluminate and potassium aluminate at a pH in the range between 5.5 and 8.0 and a temperature in the range between 20°C and 90°C, wherein step b) comprises ageing the precipitate at a temperature ranging from 20°C to 90°C for at least 15 minutes at a pH ranging from 11.0 to 12.0, and wherein step d) comprises mixing the precipitate with one or more solution(s) containing solubilized molybdate or dimolybdate salts and nickel or cobalt salts, and phosphoric acid in an amount of from 0.2 to 1.5 moles of phosphorus per mole of molybdenum at a pH in the range between 4.0 and 6.0 and a temperature in the range between 25°C and 100°C until adsorption of the metal salts onto the gel is sufficient to yield a final catalyst having from 10%w to 14%w molybdenum and from 2.5%w to 4%w nickel or cobalt.

12. A catalyst which comprises a catalytically effective amount of an element selected from the group consisting of nickel, cobalt and mixtures thereof, and a catalytically effective amount of a heavy metal selected from the group consisting of molybdenum, tungsten and mixtures thereof on an alumina support, said catalyst having a surface area greater than 300 m<sup>2</sup>/g and at least 80% of its pore volume in pores having diameters less than 5 nm, and wherein said catalyst is prepared by a process of claims according to any one of 1-11.

13. A process for hydrotreating hydrocarbon feeds, wherein use is made of a catalyst as claimed in claim 12.

## Patentansprüche

1. Ein Verfahren zur Herstellung von für die Hydrobehandlung geeigneten Katalysatoren mit Oberflächenausdehnungen von mehr als 300 m<sup>2</sup>/g und Porendurchmessern, die zu mindestens 80% kleiner sind als 5 nm, welches Verfahren die Schritte umfaßt:

(a) Ausfällen einer wäßrigen Lösung eines oder mehrerer Aluminiumsalze(s) durch Einstellen des pH-Wertes der genannten Lösung auf einen Bereich zwischen 5,5 und 10,0 bei einer Temperatur im Bereich zwischen 20°C und 90°C, unter Bildung eines Niederschlags,

(b) Altern des Niederschlags bei einer Temperatur im Bereich von 20°C bis 90°C über einen Zeitraum von mindestens 15 Minuten bei einem pH-Wert im Bereich von 11,0 bis 12,5,

(c) Waschen des Niederschlags,

(d) Mischen des Niederschlags mit einer oder mehreren Lösung(en), enthaltend solubilisierete Salze eines Schwermetalls, ausgewählt aus der Gruppe bestehend aus Molybdän, Wolfram und Mischungen davon und ein Element, ausgewählt aus der Gruppe bestehend aus Nickel, Kobalt und Mischungen davon, und eine phosphorhaltige Verbindung in einer Menge von 0,2 bis 1,5 Mol Phosphor pro Mol Schwermetall bei einem pH-Wert im Bereich zwischen 4,0 und 8,0 und einer Temperatur im Bereich zwischen 25°C und 100°C, bis die Metallsalze an dem Gel ausreichend adsorbiert sind, so daß ein Endkatalysator mit 8 bis 32 Gewichtsprozent Schwermetall und 1 bis 5 Gewichtsprozent Nickel und/oder Kobalt erhalten wird,

(e) Extrudieren des in Stufe (d) erhaltenen Produkts, und



(f) Trocknen und Calzinieren des in Stufe (e) erhaltenen Produkts bei einer Temperatur im Bereich von 300°C bis 900°C.

2. Ein Verfahren nach Anspruch 1, in welchem die Stufe (a) das Bilden eines Niederschlags durch Titrieren einer wäßrigen Lösung eines sauren Aluminiumsalzes mit einer wäßrigen Lösung einer basischen Aluminiumverbindung bei einem pH-Wert im Bereich zwischen 5,5 und 10,0 und einer Temperatur im Bereich von 20°C bis 90°C umfaßt.

3. Ein Verfahren nach Anspruch 1 oder 2, in welchem das Ausfällen bei einem pH-Wert im Bereich von 5,5 bis 8,0 durchgeführt wird.

4. Ein Verfahren nach einem der Ansprüche 1 bis 3, in welchem das Ausfällen bei einer Temperatur zwischen 50°C und 85°C durchgeführt wird.

5. Ein Verfahren nach einem der Ansprüche 1 bis 4, in welchem der pH-Wert beim Altern im Bereich zwischen 11,0 und 12,0 liegt.

6. Ein Verfahren nach einem der Ansprüche 1 bis 5, in welchem die Stufe (d) bei einem pH-Wert im Bereich zwischen 4,0 und 6,0 durchgeführt wird.

7. Ein Verfahren nach einem der Ansprüche 1 bis 6, in welchem die genannte phosphorhaltige Verbindung Phosphorsäure, ein Phosphatsalz oder eine Mischung davon ist.

8. Ein Verfahren nach einem der Ansprüche 1 bis 7, in welchem der genannte Katalysator 8 bis 18 Gewichtsprozent Molybdän und 2,5 bis 4 Gewichtsprozent Nickel und/oder Kobalt enthält.

9. Ein Verfahren nach Anspruch 2, in welchem die Stufe (a) das Bilden eines Niederschlags durch Titrieren einer wäßrigen Lösung eines sauren Aluminiumsalzes, ausgewählt aus der Gruppe bestehend aus Aluminiumsulfat, Aluminiumnitrat und Aluminiumchlorid, mit einer wäßrigen Lösung einer basischen Aluminiumverbindung, ausgewählt aus der Gruppe bestehend aus Natriumaluminat und Kaliumaluminat, bei einem pH-Wert im Bereich von 5,5 bis 8,0 und einer Temperatur im Bereich zwischen 20°C und 90°C umfaßt, in welchem die Stufe (b) das Altern des Niederschlags bei einer Temperatur im Bereich von 20°C bis 90°C über einen Zeitraum von mindestens 15 Minuten bei einem pH-Wert im Bereich von 11,0 bis 12,0 umfaßt und in welchem die Stufe (d) das Mischen des Niederschlags mit einer oder mehreren Lösung(en), enthaltend solubilisierete Molybdat- oder Dimolybdat-salze und Nickel- oder Kobaltsalze, und Phosphorsäure in einer Menge von 0,2 bis 1,5 Mol Phosphor pro Mol Molybdän bei einem pH-Wert im Bereich von 4,0 bis 6,0 und einer Temperatur im Bereich zwischen 25°C und 100°C bis die Metallsalze an dem Gel ausreichend adsorbiert sind, so daß ein Endkatalysator mit 10 bis 14 Gewichtsprozent Molybdän und 2,5 bis 4 Gewichtsprozent Nickel oder Kobalt erhalten wird, umfaßt.

10. Ein Verfahren nach Anspruch 1, in welchem die Stufe (a) das Ausfällen einer wäßrigen Lösung eines sauren Aluminiumsalzes, ausgewählt aus der Gruppe bestehend aus Aluminiumsulfat, Aluminiumnitrat und Aluminiumchlorid, mit einer wäßrigen Lösung einer Base bei einem pH-Wert im Bereich von 5,5 bis 8,0 und einer Temperatur im Bereich von 20°C bis 90°C, unter Bildung eines Niederschlags umfaßt, die Stufe (b) das Altern des Niederschlags bei einer Temperatur im Bereich von 20°C bis 90°C über einen Zeitraum von mindestens 15 Minuten bei einem pH-Wert im Bereich von 11,0 bis 12,0 umfaßt und die Stufe (d) das Mischen des Niederschlags mit einer oder mehreren Lösung(en), enthaltend solubilisierete Molybdat- oder Dimolybdat-salze und Nickel- oder Kobaltsalze, und Phosphorsäure in einer Menge von 0,2 bis 1,5 Mol Phosphor pro Mol Molybdän bei einem pH-Wert im Bereich von 4,0 bis 6,0 und einer Temperatur im Bereich von 25°C bis 100°C, bis die Metallsalze an dem Gel ausreichend adsorbiert sind, so daß ein Endkatalysator mit 10 bis 14 Gewichtsprozent Molybdän und 2,5 bis 4 Gewichtsprozent Nickel oder Kobalt erhalten wird, umfaßt.

11. Ein Verfahren nach Anspruch 2, in welchem die Stufe (a) das Bilden eines Niederschlags durch Titrieren einer wäßrigen Lösung einer Säure mit einer wäßrigen Lösung einer basischen Aluminiumverbindung, ausgewählt aus der Gruppe bestehend aus Natriumaluminat und Kaliumaluminat, bei einem pH-Wert im Bereich zwischen 5,5 und 8,0 und einer Temperatur im Bereich zwischen 20°C und 90°C umfaßt, die Stufe (b) das Altern des Niederschlags bei einer Temperatur im Bereich von 20°C bis 90°C über einen Zeitraum von mindestens 15 Minuten bei einem pH-Wert im Bereich von 11,0 bis 12,0 umfaßt und die Stufe (d) das Mischen des Niederschlags mit einer oder mehreren Lösung(en), enthaltend solubilisierete Molybdat- oder Dimolybdat-salze und Nickel- oder Kobaltsalze, und Phosphorsäure in einer Menge von 0,2 bis 1,5 Mol Phosphor pro Mol Molybdän bei einem pH-Wert im Bereich zwischen 4,0 und 6,0 und bei einer Temperatur im Bereich von 25°C bis 100°C, bis die Metallsalze ausreichend an dem Gel adsorbiert sind, so daß ein Endkatalysator mit 10 bis 14 Gewichtsprozent Molybdän und mit 2,5 bis 4 Gewichtsprozent Nickel oder Kobalt erhalten wird, umfaßt.

12. Ein Katalysator, der eine katalytisch wirksame Menge eines Elementes, ausgewählt aus der Gruppe bestehend aus Nickel, Kobalt und Mischungen davon, und eine katalytisch wirksame Menge eines Schwermetalls, ausgewählt aus der Gruppe bestehend aus Molybdän, Wolfram und Mischungen davon, auf einem Aluminiumoxidträger enthält, wobei dieser Katalysator eine Oberflächenausdehnung von mehr als 300 m<sup>2</sup>/g hat und sein Porenvolumen zu mindestens 80% aus Poren mit einem Durchmesser von weniger als 5 nm besteht, und wobei dieser Katalysator durch ein Verfahren nach einem der Ansprüche 1 bis 11 hergestellt worden ist.

13. Ein Verfahren zur Hydrobehandlung von Kohlenwasserstoffeinsatzmaterial, in welchem ein Katalysator wie in Anspruch 12 beansprucht verwendet wird.



## Revendications

1. Un procédé de préparation de catalyseurs d'hydrotraitement ayant des surfaces spécifiques de plus de 300 m<sup>2</sup>/g et au moins 80% des diamètres de pores inférieurs à 5 nm, procédé qui comprend:

- (a) la précipitation d'une solution aqueuse d'un ou plusieurs sels d'aluminium par ajustement du pH de cette solution à un intervalle compris entre 5,5 et 10,0 et à une température comprise entre 20°C et 90°C, de manière à former un précipité,
- (b) le vieillissement du précipité à une température comprise entre 20°C et 90°C pendant au moins 15 minutes à un pH compris entre 11,0 et 12,5,
- (c) le lavage du précipité,
- (d) le mélange du précipité avec une ou plusieurs solutions contenant des sels solubilisés d'un métal lourd choisi dans le groupe constitué par le molybdène, le tungstène et leurs mélanges et d'un élément choisi dans le groupe constitué par le nickel, le cobalt et leurs mélanges, et un composé contenant du phosphore à raison de 0,2 à 1,5 mole de phosphore par mole de métal lourd à un pH compris entre 4,0 et 8,0 et à une température comprise entre 25°C et 100°C jusqu'à ce que l'adsorption des sels de métaux sur le gel soit suffisante pour donner un catalyseur final ayant de 8% en poids à 32% en poids de métal lourd et de 1% en poids à 5% en poids de nickel et/ou de cobalt,
- (e) l'extrusion du produit de l'étape (d) et
- (f) le séchage et la calcination du produit de l'étape (e) à une température comprise entre 300°C et 900°C.

2. Un procédé selon la revendication 1, dans lequel l'étape a) comprend la formation d'un précipité en titrant une solution aqueuse d'un sel acide d'aluminium avec une solution aqueuse d'un sel basique d'aluminium à un pH compris entre 5,5 et 10,0 et à une température comprise entre 20°C et 90°C.

3. Un procédé selon la revendication 1 ou 2, dans lequel la précipitation est effectuée à un pH compris entre 5,5 et 8,0.

4. Un procédé selon l'une quelconque des revendications 1-3, dans lequel la précipitation est effectuée à une température comprise entre 50°C et 85°C.

5. Un procédé selon l'une quelconque des revendications 1-4, dans lequel le pH de vieillissement est compris entre 11,0 et 12,0.

6. Un procédé selon l'une quelconque des revendications 1-5, dans lequel l'étape d) est conduite à un pH compris entre 4,0 et 6,0.

7. Un procédé selon l'une quelconque des revendications 1-6, dans lequel le composé contenant du phosphore est de l'acide phosphorique, un sel d'acide phosphorique ou un mélange de tels composés.

8. Un procédé selon l'une quelconque des revendications 1-7, dans lequel le catalyseur contient de 8% en poids à 18% en poids de molybdène et de 2,5% en poids à 4% en poids de nickel et/ou de cobalt.

9. Un procédé selon la revendication 2, dans lequel l'étape a) comprend la formation d'un précipité en titrant une solution aqueuse d'un sel acide d'aluminium choisi dans le groupe constitué par le sulfate d'aluminium, le nitrate d'aluminium et le chlorure d'aluminium avec une solution aqueuse d'un composé basique d'aluminium choisi dans le groupe constitué par l'aluminate de sodium et l'aluminate de potassium, à un pH compris entre 5,5 et 8,0 et à une température comprise entre 20°C et 90°C, l'étape b) comprend le vieillissement du précipité à une température comprise entre 20°C et 90°C pendant au moins 15 minutes à un pH compris entre 11,0 et 12,0 et l'étape d) comprend le mélange du précipité avec une ou plusieurs solutions contenant des sels lyophilisés molybdates ou dimolybdates et des sels de nickel ou de cobalt et de l'acide phosphorique à raison de 0,2 à 1,5 mole de phosphore par mole de molybdène à un pH compris entre 4,0 et 6,0 et à une température comprise entre 25°C et 100°C jusqu'à ce que l'adsorption des sels de métaux sur le gel soit suffisante pour donner un catalyseur final ayant de 10% en poids à 14% en poids de molybdène et de 2,5% en poids à 4% en poids de nickel ou de cobalt.

10. Un procédé selon la revendication 1, dans lequel l'étape a) comprend la précipitation d'une solution aqueuse d'un sel acide d'aluminium choisi dans le groupe constitué par le sulfate d'aluminium, le nitrate d'aluminium et le chlorure d'aluminium avec une solution aqueuse d'une base à un pH compris entre 5,5 et 8,0 et à une température comprise entre 20°C et 90°C, de manière à former un précipité, l'étape b) comprend le vieillissement du précipité à une température comprise entre 20°C et 90°C pendant au moins 15 minutes à un pH compris entre 11,0 et 12,0 et l'étape d) comprend le mélange du précipité avec une ou plusieurs solutions contenant des sels solubilisés molybdates ou dimolybdates et des sels de nickel ou de cobalt et de l'acide phosphorique à raison de 0,2 à 1,5 mole de phosphore par mole de molybdène à un pH compris entre 4,0 et 6,0 et à une température comprise entre 25°C et 100°C jusqu'à ce que l'adsorption des sels de métaux sur le gel soit suffisante pour donner un catalyseur final ayant de 10% en poids à 14% en poids de molybdène et de 2,5% en poids à 4% en poids de nickel ou de cobalt.

11. Un procédé selon la revendication 2, dans lequel l'étape a) comprend la formation d'un précipité en titrant une solution aqueuse d'un acide avec une solution aqueuse d'un composé basique d'aluminium choisi dans le groupe constitué par l'aluminate de sodium et l'aluminate de potassium à un pH compris entre 5,5 et 8,0 et à une température comprise entre 20°C et 90°C, l'étape b) comprend le vieillissement du précipité à une température comprise entre 20°C et 90°C pendant au moins 15 minutes à un pH compris entre 11,0 et 12,0 et l'étape d) comprend le mélange du précipité avec une ou plusieurs solutions contenant des sels solubilisés molybdates ou dimolybdates et des sels de nickel ou de cobalt, et de l'acide

phosphorique à raison de 0,2 à 1,5 mole de phosphore par mole de molybdène à un pH compris entre 4,0 et 6,0 et une température comprise entre 25°C et 100°C jusqu'à ce que l'adsorption des sels de métaux sur le gel soit suffisante pour donner un catalyseur final ayant de 10% en poids à 14% en poids de molybdène et de 2,5% en poids à 4% en poids de nickel ou de cobalt.

- 5 12. Un catalyseur qui comprend une quantité catalytiquement efficace d'un élément choisi dans le groupe constitué par le nickel, le cobalt et leurs mélanges et une quantité catalytiquement efficace d'un métal lourd choisi dans le groupe constitué par le molybdène, le tungstène et leurs mélanges sur un support d'alumine, ce catalyseur ayant une surface spécifique supérieure à 300 m<sup>2</sup>/g et au moins 80% de son volume de pores dans des pores ayant des diamètres de moins de 5 nm, ce catalyseur étant préparé par un
- 10 procédé selon l'une quelconque des revendications 1-11.

13. Un procédé d'hydrotraitement de charges hydrocarbonées, dans lequel on utilise un catalyseur selon la revendication 12.

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